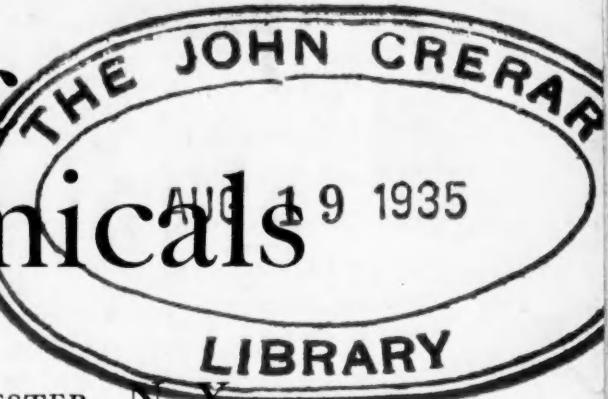


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# Synthetic Organic Chemicals

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## CHLOROPHYLL

**I**N THE chloroplasts of plants there are four groups of pigments in colloidal mixture with colorless substances of high molecular weight. These four groups of pigments are the chlorophylls (*a* and *b*)—the green pigments—and the carotenes and xanthophylls—the yellow ones. The average chlorophyll content of fresh leaves is between one and two one-thousandths of the total weight.

The first chemical investigations of chlorophyll date back to Berzelius who, in 1839, attempted to isolate the pigment from leaves. Thinking that he had a pure product and that it was not materially affected by acid or alkaline solutions, he treated the alcoholic extract so vigorously that he obtained only degradation products. Since then, many chemical investigations have been published, most of which have been based upon spectroscopic studies, but there seemed to be no consistent results among different workers. It was, therefore, concluded that various plants contained different kinds of chlorophyll, since all the investigators had not isolated their products from the same plant. Etard, in fact, claimed (1906) that one plant alone (*Lolium perenne*) contained no less than six different varieties, having considered each fraction of the waxy material extracted a pure chlorophyll.

Willstätter, in his brilliant researches of the first decade of this century, de-

veloped a method for isolating chlorophyll from the xanthophyll and carotene. The method, which is still employed, is based upon an extraordinary technique in the use of certain organic solvents and their relative distribution coefficients in aqueous solutions. After a careful examination of the chlorophyll obtained from over two hundred different kinds of plants, he was quite justified in concluding that there was only one chlorophyll which exists in two forms, designated as the *a* and *b* components. Furthermore, Willstätter devised for separating these two components a method which depends upon their partition between petroleum ether and methyl alcohol: component *a* goes into the petroleum ether; component *b*, into the methyl alcohol phase.

The differences in the two components of chlorophyll by analysis are indicated by the following formulae:

chlorophyll *a*  $C_{55}H_{72}N_4O_5Mg$

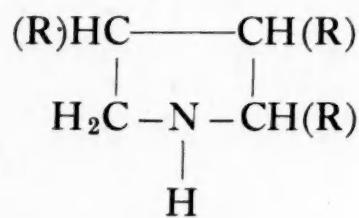
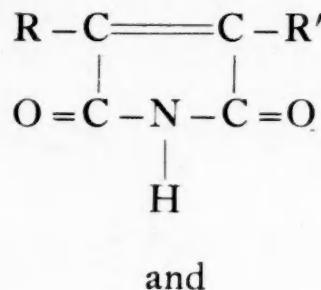
chlorophyll *b*  $C_{55}H_{70}N_4O_6Mg$

Each component yields a separate series of degradation products; both, when acted upon by extremely mild hydrolyzing agents, yield an unsaturated alcohol, phytol ( $C_{20}H_{39}OH$ ), which constitutes about thirty per cent of the chlorophyll molecule.

The structure of this alcohol was definitely established about 1926 and

has a skeleton represented by four isoprene units placed end to end. Hydrolysis with cold, dilute, caustic potash gives equimolecular quantities of the two alcohols, methyl and phytol, and of chlorophyllin,  $C_{31}H_{30}N_4Mg(CO)(COOH)_2$ . Thus, chlorophyll *a* may be considered as methyl phytol chlorophyllin. Chlorophyllin can form a tripotassium carboxylic acid salt,  $C_{31}H_{31}N_4Mg(COOK)_3$ , and, therefore, the fifth oxygen of chlorophyll must be assumed to exist as a potential carboxyl group in the form of a lactam or an inner anhydride.

Upon more drastic treatment with alkali at higher temperatures, chlorophyllin *a* yields a series of phyllins, due to the stepwise loss of carbon dioxide. These phyllins in turn, when treated gently with acids (e.g., alcoholic oxalic acid), yield a series of products belonging to the interesting and widespread class of substances called the porphyrins. Upon oxidation and reduction, the porphyrins yield substituted maleimides and pyrrolidines, respectively:



This suggests that the skeleton structure of the porphyrins is made up of pyrrole nuclei. And, since all porphyrins contain four atoms of nitrogen, Will-

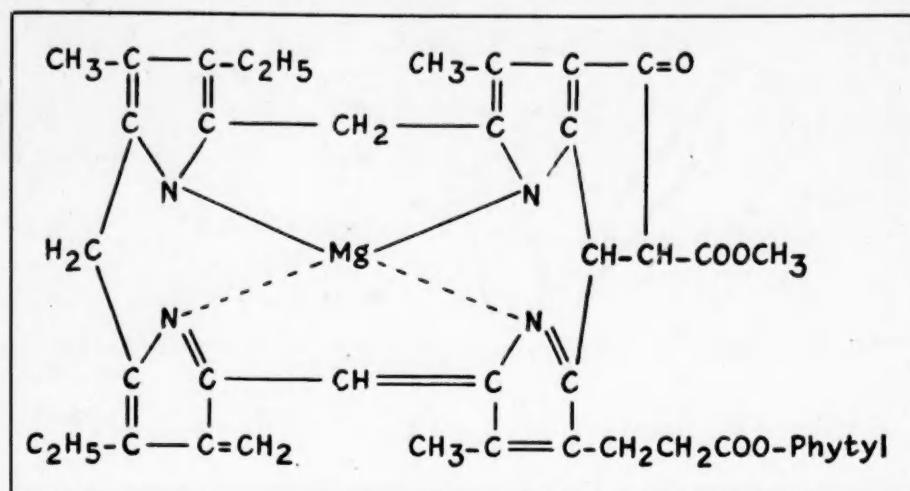
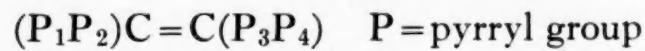
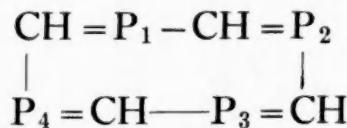


FIGURE 1

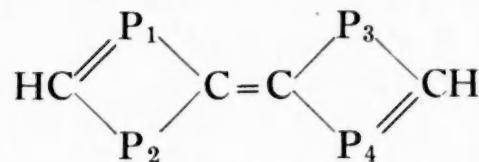
stätter (1910) proposed the structure of a tetra-substituted pyrryl ethylene:



Küster (1911) suggested the following structure:



Willstätter, however, believed that such a large ring structure was entirely out of the question (on the basis of the Baeyer's strain theory). Hans Fischer compromised, proposing a structure:



Each investigator set about preparing his proposed tetrapyrrolic compound, hoping that it would be a porphyrin. Fischer succeeded in preparing substances represented by Willstätter's formula, but they did not have the characteristic spectra of true porphyrins. In 1926, after nearly fourteen years, Fischer finally obtained a substance having the properties of a porphyrin. Interestingly enough, the sixteen-membered ring structure proposed by Küster proved to be the correct one.

Since that time, Fischer and his co-workers have synthesized hundreds of porphyrins, among them actual degradation products of chlorophyll itself.

Recently, the formula for chlorophyll *a* which is given in Figure 1 was proposed by them. While this structure is correct in all major respects, it must be pointed out that a few minor details are still in question.

At present, the work on the structure of chlorophyll *b* is progressing rapidly in a number of laboratories throughout the world, and it will probably not be long before the entire story of this important pigment will be revealed.

## Eastman Organic Chemicals as Analytical Reagents

### XXXVIII REAGENTS FOR HALOGENS

#### BROM PHENOL BLUE

Kolthoff and Larson, J.A.C.S., 56, 1881 (1934)

Chlorides or bromides in concentrations greater than 0.04 N and 0.01 N, respectively, can be titrated accurately with mercurous nitrate by using brom phenol blue as an absorption indicator. The indicator remains in the yellow form when there is an excess of the halide present, and is absorbed with a lilac color in the presence of an excess of mercury. A 0.1% aqueous solution of the mono sodium salt of the indicator is used.

#### PHENOL RED

Stenger and Kolthoff, J.A.C.S., 57, 831 (May, 1935)

Minute quantities of bromide can be determined by means of phenol red in the presence of calcium hypochlorite. Under these conditions, phenol red with a color change from yellow at 6.8 to red at 8.4 reacts with dilute hypobromite to form an indicator of the brom phenol blue type. The reaction is carried out in a borax buffer at pH 8.7-8.8.

The completely brominated product, tetrabromophenolsulfonphthalein (brom phenol blue), has a color change from yellow at pH 3 to blue at 4.7. By making the color comparison at pH 5.0-5.4

(acetate buffer), all the unbrominated phenol red and any trace of chlor phenol red will be in yellow form, whereas the brominated compound will be reddish to violet depending upon its concentration. Chlorides do not interfere, but iodides must be removed. Reducing agents must be removed or oxidized.

#### FUCHSIN

R. Casares Lopez, Farm. moderna, 46, 55-57 (1935); Ann. fals., 28, 115-16.

Very slight traces of bromide in sodium chloride solutions can be detected by means of fuchsin. To 10 cc. of water in a test tube is added one drop of saturated fuchsin solution (0.2%) and then Cl<sub>2</sub> solution (about .0024 gm. Cl per cc.), drop by drop, to complete decolorization. About 6 to 8 drops are usually required. The test is carried out by adding to the solution to be tested one drop of fuchsin and twice the number of drops of Cl solution previously determined as necessary to decolorize the fuchsin.

In the presence of Br, a pink color is obtained which, if sufficient bromine is present, turns violet with ultimate formation of a violet precipitate. The test will detect .0001 g. KBr in 10 cc. of 20% NaCl solution, equivalent to 3 mg. Br per 100 g. NaCl.

**Plan to attend the Sixth National Organic Chemistry Symposium**  
Rochester, N. Y., December 30, 1935—January 1, 1936

## New Eastman Organic Chemicals

In line with the policy of continually increasing the number of organic chemicals available to American chemists, twenty new compounds have been added to the stock of Eastman Organic Chemical catalog since the publication of List No. 26 in April, 1935.

One of the most interesting of these new compounds is 4001 d-Lyxose. It is a pentose, stereo-isomeric with arabinose, xylose, and ribose, and has the general formula  $\text{CH}_2\text{OH}(\text{CHOH})_3\text{CHO}$ . Its addition to the list makes available the four known isomeric aldopentoses, eight of which can theoretically exist. Although specified as d-Lyxose according to the system originally suggested by E. Fischer, it actually is laevo rotatory. According to the literature, at 20° C. the optical rotation with the sodium line is  $-3.1^\circ$  four minutes after solution, finally reaching a constant value of  $-13.9^\circ$ . The purity of the present stock

is indicated by its rotation of  $-14^\circ$ .

Several years ago work was started on the preparation of new heterocyclic compounds, resulting in the addition to the list of many interesting products. This group has been augmented by others of this same type, among which are 3834 2,4-Dimethyl-3,5-dicarbethoxypyrrrole; 3967 1-Benzothiazolylhydrazine; 2406 6-Nitrobenzimidazole; and 2784 1-Chlorobenzothiazole.

Naringin, supplied in a practical grade as a brownish powder, should prove interesting as it is the bitter constituent present in grapefruit. The series of polymethylene glycols has been extended by the addition of 4025 Hexamethylene Glycol.

The chlorine in 2801  $\alpha$ -Chloroquinoline is very reactive, and the compound should prove of value in synthesizing a variety of new compounds.

4023	Aminoguanidine Sulfate	100 g.	\$ 7.00	C
P 3968	p-Aminophenylacetonitrile Hydrochloride (Practical)	100 g.	8.00	C
3967	1-Benzothiazolylhydrazine MP 197-198°	100 g.	12.00	C
4009	2-Bromopyridine BP 76-80°/14 mm.	10 g.	3.00	A
T 785	iso-Butyric Acid (Technical) BP 144-154°	1 kg.	7.50	E
2784	1-Chlorobenzothiazole BP 130-131°/18 mm.	100 g.	4.00	C
2801	$\alpha$ -Chloroquinoline MP 36-38°	100 g.	12.00	C
P 3819	Difurfural Cyclopentanone (Practical) MP 158-163°	1 kg.	2.50	E
3834	2,4-Dimethyl-3,5-dicarbethoxypyrrrole MP 134-135°	10 g.	4.00	A
3954	unsym.-Dimethylhydrazine Hydrochloride MP 81-82°	10 g.	3.00	A
4025	Hexamethylene Glycol MP 40-42°	10 g.	2.00	A
4001	d-Lyxose	1 g.	2.00	A
3953	Methylhydrazine Sulfate MP 141-142°	10 g.	3.00	A
3976	N-Methylquinolone MP 72-74°	100 g.	8.00	C
P 3996	Naringin (Practical)	500 g.	13.50	D
2406	6-Nitrobenzimidazole MP 204-206°	1 g.	4.00	O
3906	2-Nitrodiphenylamine MP 75-76°	100 g.	7.00	C
3957	4-Nitrophthalimide	100 g.	4.00	C
3969	Potassium 4-Nitrophthalimide	100 g.	4.00	C
P 4026	Sucrose Octaacetate (Practical) MP 72-74°	2 kg.	3.50	G